

FINAL TECHNICAL REPORT

**MULTI-FUNCTIONAL π -CONJUGATED MACROMOLECULES
BASED ON POLY(PHENYLENE VINYLENE)**

DIELECTRIC STRENGTHS/DENDRITIC POLYMERS

GRANT AFOSR F49620-93-1-0178

March 15, 1993 - March 14, 1996

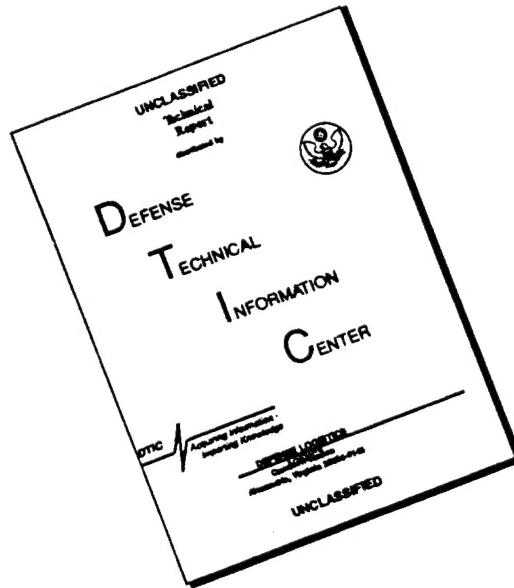
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- I. TITLE: (1) Multi-Functional π -Conjugated Macromolecules Based on Poly(Phenylene Vinylene) (2) Dielectric Strengths/Dendritic Polymers
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VI. ABSTRACT OF ACCOMPLISHMENTS

Numerous investigations of the synthesis, structures and properties of polyphenylene vinylene (PPV) and related macromolecules with novel electro-optical characteristics have been completed. Novel homopolymers and copolymers of varying architecture have been designed and synthesized and shown to be highly efficient chromophores in electroluminescent devices. Other polymers which have been synthesized and characterized include side-chain liquid crystalline systems with systematically varying mesogens, and novel high temperature polyimides. The study of the phase behavior of polymer blends has continued with emphasis on sequence distribution effects in the respective copolymer constituent(s) and on detailed probes of the structure of miscible systems using advanced solid state NMR techniques. Dynamic light scattering studies of solvated flexible polymer chains in confined geometries (e.g. pores) have led to new insights into transport phenomena for such systems and to proposals for novel fractionation. A series of hyperbranched polyarylates have been prepared and studied with respect to their structure and properties both in solution and in the solid state, and in blends with linear chains. Additional theoretical investigating of transition, surface and bulk properties of single and multi-component polymer systems including simulation studies have been completed.

VII. DESCRIPTION OF RESEARCH UNDERTAKEN

The grant has supported several lines of research in the physical chemistry of macromolecules, including some continuing from earlier AFOSR funding. The results have in large part been published in the open literature, as discussed below.

A. π -Conjugated Macromolecules: Synthesis and Structure (1, 22, 28, 32, 34, 35, 37, 38, 40, 48, 58, 60, 65, 74¹)

Studies of the syntheses and properties of π -conjugated polymers centered around the polyphenylene vinylene (PPV) structure has been a focus here for over fifteen years. In this grant period these include new techniques which have been developed for the detailed elucidation of the solid state structure of PPV and of doped (oxidized/reduced) PPV and of its analogs and derivatives. PPV is a prototypical π -conjugated macromolecule which displays multiple functions such as high electrical conductivity, non-linear optical properties and photo- and electroluminescence, and thus an understanding of the solid state structure and behavior is key to developing relationships between chemical architecture and these important properties. Solid state NMR of selectively deuterated PPV has been found to yield highly detailed structural information comparable to that obtainable by x-ray techniques, though the latter has also been used to study the precise variations in structure on doping with alkali metals and other small molecules. Inelastic

¹The numbers in the section headings correspond to the publications listed in Section VIII.

neutron scattering has served to probe additional structural aspects.

The properties of PPV can be conveniently modulated in an extremely versatile fashion by derivatization, heterocycle analog substitution and other accessible chemical modifications. In some cases these structures can be achieved through slight variations of the classical Wessling polyelectrolyte precursor synthesis, in others more radical changes are required as a result of reaction rate modifications brought about by the derivatization. Large numbers of PPV variations have been systematically synthesized both in order to gain an understanding of the basic polymerization mechanisms and to prepare materials for specific applications.

Conspicuous amongst the latter motivation has been the syntheses of segmented block copolymers containing oligomeric phenylene vinylene (or variations thereof) sequences interspersed with "soft blocks" of methylene segments. These polymers have been used in electroluminescent devices (see below, B) and their synthesis has departed from Wessling chemistry, using alternatively Wittig phosphonium intermediates. Other properties of these π -conjugated systems of more complex architecture have also been investigated, including electrical and doping characteristics.

B. π -Conjugated Macromolecules: Electroluminescence (10, 26, 48, 49, 63, 64, 66, 68, 75, 76, 77, 82)

Polymer light emitting diodes (PLEDs) based on PPV were first demonstrated about five years ago. Major improvements have been developed

here in terms of materials and device architecture. The basic chromophore design that has been employed is the segmented block copolymer containing PPV (or PPV-related) oligomers described above. The major advantages of these materials compared to PPV include a) controlled conjugation length and thereby control of emitting wavelength b) tunability of emitting wavelength by ready chemical modification c) solubility of polymer facilitating device fabrication by spin-casting and d) improved confinement of excitons generated by double carrier injection in quantum-well size chromophore clusters, thereby enhancing efficiency and brightness (in some cases by orders of magnitude).

These improvements have evolved systematically over the course of the present grant. Their initial embodiment (publication 10, Section VIII) resulted in the first blue light emitting LED that had at that time been reported. Device architectures have also evolved. More complex three layer PLEDs utilizing a variety electron- and hole-blocking layers greatly improved the characteristics of these devices while more recently (82) it has been found that these functions could in some cases be achieved by blending (rather than layering) of the appropriate macromolecules in the device. This permits a more facile, simpler, fabrication which has obvious technological implications. Efficient PLEDs with outputs in the range of 10^3 candelas/m² and up, and covering the whole visible light spectrum have now been achieved here. Further improvements in lifetimes, etc. will require further refinements and more sophisticated facilities including clean rooms, etc.

C. Polymer Blends (11, 12, 19, 20, 23, 27, 30, 36, 42, 43, 44, 51, 52, 54, 62, 70, 78, 79, 80, 81)

Polymer-polymer miscibility has been a focus of AFOSR-supported research here for over twenty-five years. In recent years a major thrust has been on the thermodynamics and phase behavior of polymer blends as a function of the microstructure of the constituents. The first-order mean field theory for random copolymer-copolymer systems developed here has been widely used here and elsewhere in quantitative assessments of miscibility phenomena for such cases. Advanced solid state NMR techniques have been developed which have led to a better understanding of the morphology of miscible and immiscible polymer blends at the nanometer level. New theoretical advances have been made which take into account non random sequence-distribution effects of comonomer units in the constituent structure. These have been used in comparisons, for example, of a given random and alternating copolymer in terms of miscibility behavior.

D. Dynamic Light Scattering (3, 14, 16, 18, 29, 33, 45, 50, 59, 72)

Experimental techniques for dynamic light scattering have been refined so that transport properties of solvated macromolecules in confined geometries can be studied. In practice, controlled pore size silica and other glasses immersed in the appropriate polymer solutions have generally been used in such investigations. Extensive investigations of diffusion behavior as a function of solute and solvent type, of molecular weight, solute concentration

(including concentrated regimes) and the presence of second polymer components have been carried out and have provided a completely new understanding of the effect of confining geometries on transport phenomena of polymers. In addition, this work has led to a novel technique for polymer fractionation that is now being developed.

E. Liquid Crystalline Polymers (5, 6, 9, 17, 21, 24, 31, 53, 55, 71, 73)

In earlier AFOSR-supported research multifunctional polymers copolymers which incorporated mesogenic side groups were investigated. This work was continued during the present grant period and a substantial number of new insights have been obtained. The principal aims have been to gain an understanding of the physical properties, especially thermal behavior and morphology of these systems as a function of side group architecture. The typical systems studied consisted of a flexible chain backbone to which were coupled short stiff chromophoric side groups. Properties were also studied as a function of degree of substitution and of sequence distribution effects.

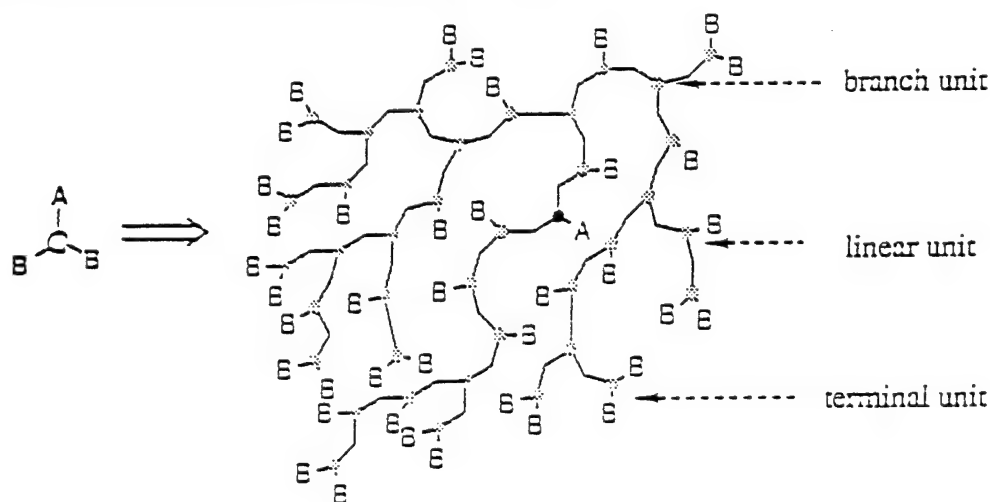
Novel polyester liquid crystal structures containing crown ether mesogens have been synthesized and characterized as well as a variety of stilbene (and stilbene analog) containing siloxane and other polymers designed specifically for electro-optical studies. A number of these polymers display significant electroluminescent activity.

F. Dendritic Polymers

A new thrust focused on dendritic/hyperbranched polymer was initiated

during the present grant period. This has resulted in the moderate scale synthesis and property evaluation of a series of polyarylates. At the time of writing, the results are only available in a doctoral thesis (Ph.D. Thesis, B. Ma, University of Massachusetts, September, 1996) and therefore a fuller description is given below.

Hyperbranched polymers are highly branched macromolecules based on AB_x ($x \geq 2$) type monomers in which A may condense with B, but reactions between like functional groups are forbidden, see Figure.

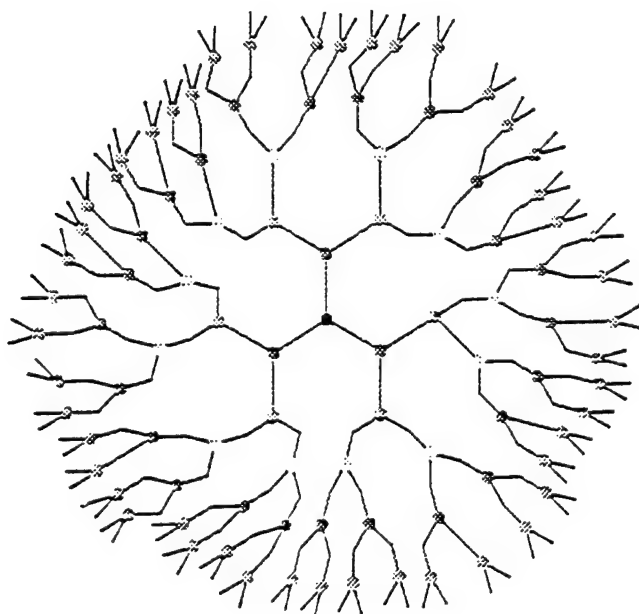


Three types of units can be identified in the above structure, branch, linear and terminal unit. The "degree of branching" is defined to measure the branching density of the structure.

$$\text{Degree of Branching} = \frac{\text{branch units} + \text{terminal units}}{\text{branch units} + \text{terminal units} + \text{linear units}}$$

Hyperbranching molecular topology has not been investigated in detail, in contrast to dendritic polymers and microgels. These three polymer groups share

Dendritic polymers are synthesized via a controlled strategy and in principle has a generationalized perfect structure. The degree of branching of dendritic polymers according to the previous definition is always 100%. There is no linear unit in the structure. Because of this highly controlled topology, there exists a molecular weight limit above which the perfect growth of an additional generation can not be accomplished.



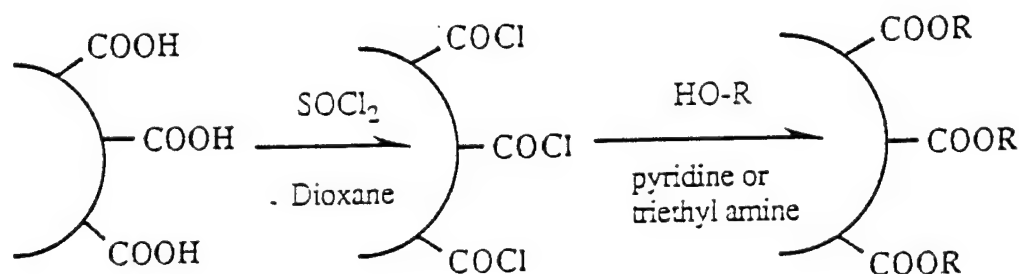
Microgels are crosslinked polymer networks usually synthesized by emulsion polymerization process. Because of the presence of a network, the branch unit content is always greater than 50% unlike the other two polymer groups. There is also no limit for the growth of individual microgel particles.

Only a few AB_2 type monomers have been polymerized to form hyperbranched polymers. These derivatives include poly(aryl ester)s, polyethers, polyamines,

material, such as rheology and miscibility with other polymers.

For the purpose of this investigation, substantial quantities of hyperbranched polyarylates based on 5-acetoxisophthalic acid were required. To achieve this goal and to avoid a heat transfer problem suspension polymerization was used, instead of a melt process.

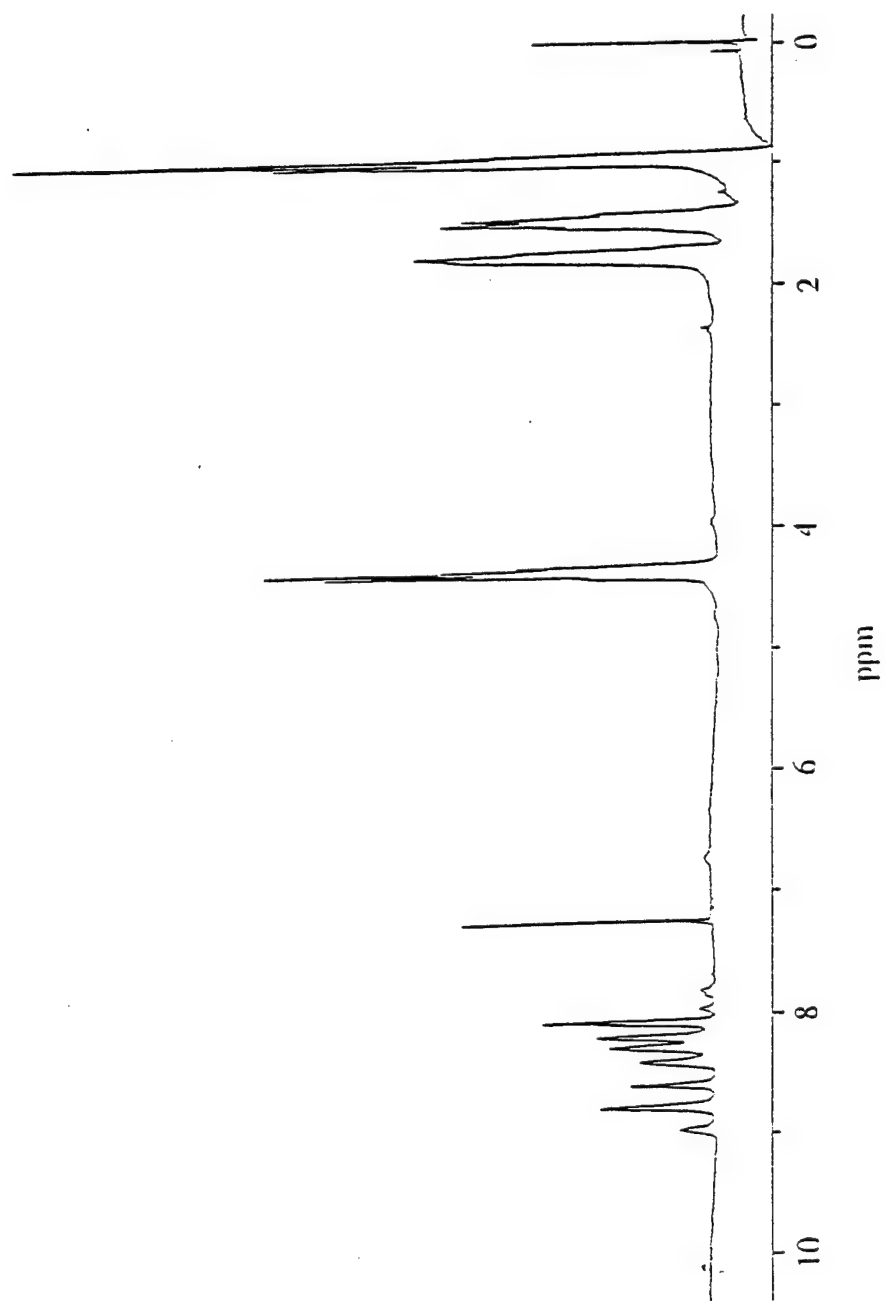
The residual carboxyl groups remaining in the hyperbranched structure were further modified through acyl chloride intermediates.



Several modified products were made with this procedure including methyl, phenyl, n-butyl and 2-ethylhexyl hyperbranched polyarylates, abbreviated as MeHP, PhHP, BuHP and EhHP respectively.

Various techniques were employed to characterize the resulting materials. Examples are shown in the attached figures.

The effect of hyperbranching topology on the miscibility and compatibility of blends containing these materials was also studied. For example, the miscibility of BuHP and poly 1,4-butylene isophthalate (PBI) was investigated thermally, by TEM and in terms of rheological parameters.



^1H NMR of BuIP

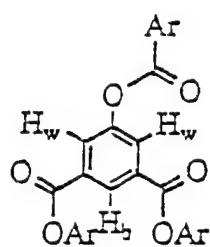
Fractionation Results of Hyperbranched Polyarylates^a

Sample No.	2-Ethylhexyl Ester ^b		Phenyl Ester ^c		Methyl Ester ^c		n-Butyl Ester ^c	
	$M_n (\times 10^4)$	PDI	$M_n (\times 10^4)$	PDI	$M_n (\times 10^4)$	PDI	$M_n (\times 10^4)$	PDI
1	0.126	1.16	3.58	1.23	4.28	1.29	0.235	1.39
2	0.251	1.19	6.51	1.30	6.35	1.24	0.363	1.44
3	0.437	1.33	7.64	1.35	9.71	1.27	0.647	1.37
4	0.603	1.34	10.5	1.26	10.3	1.33	0.724	1.43
5	0.832	1.37	14.2	1.36	15.5	1.36	0.775	2.13
6	1.12	1.27	21.1	1.51	40.7	1.58	2.68	2.58
7	1.41	1.29	26.0	1.73	50.4	1.85	5.84	2.85
8	1.91	1.32	34.2	1.82	82.6	2.06	9.24	3.06
9	2.14	1.34	47.3	2.06	103	3.35	12.6	4.35
10	2.40	2.19	55.0	2.43	126	3.57	17.3	4.57
11	3.47	2.78	108	3.56				
12	13.8	2.83	183	4.48				
13	17.8	3.42	294	4.57				

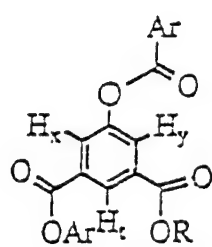
a. Starting condition: $PDI = M_w/M_n > 10.0$

b. By preparative GPC method

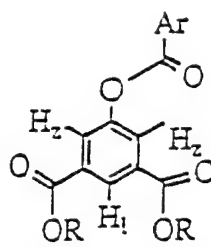
c. By precipitation method



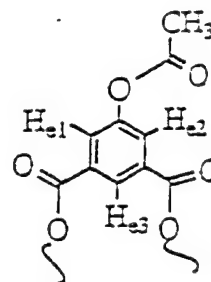
branch unit



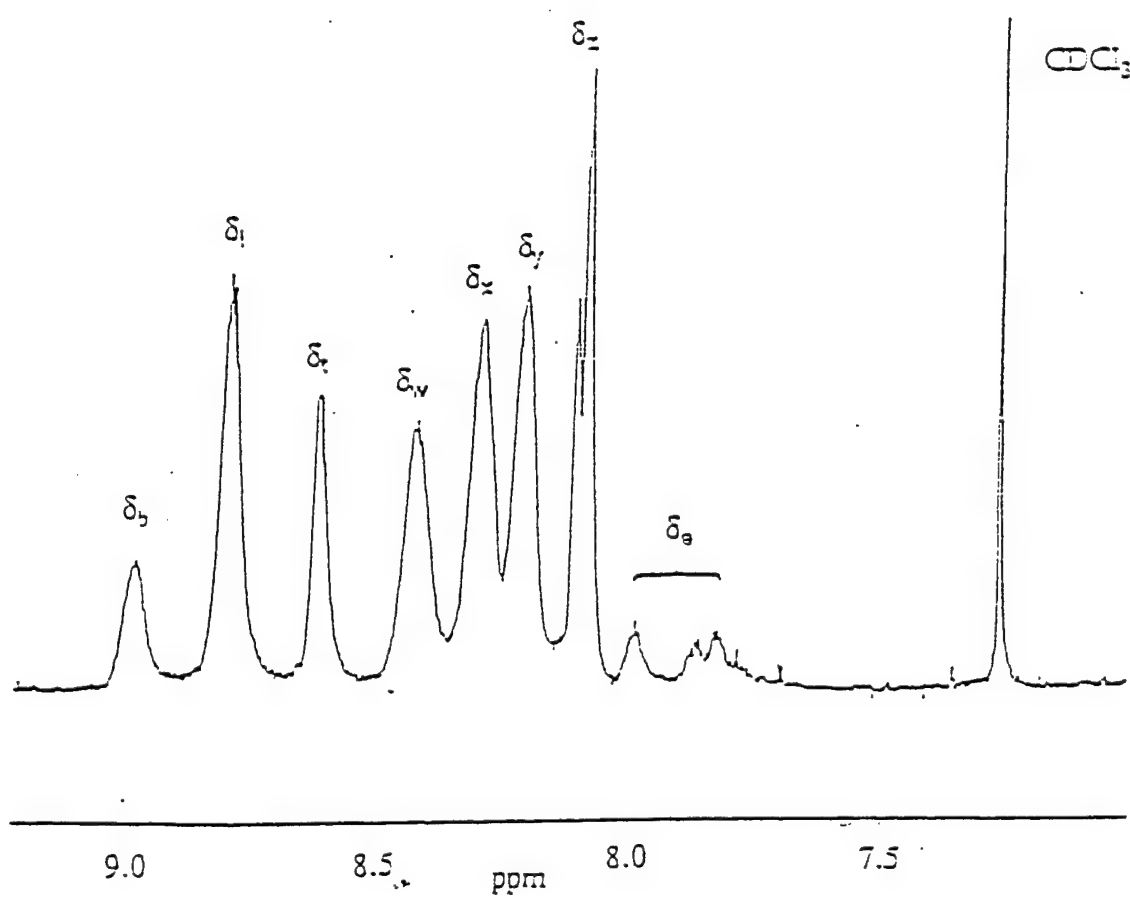
linear unit



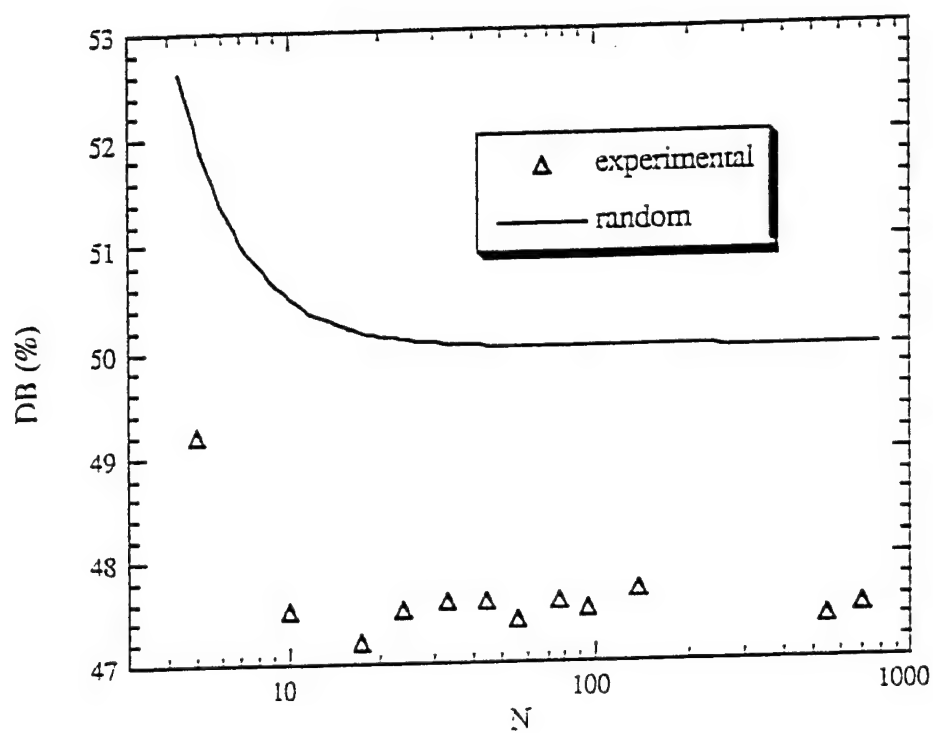
terminal unit



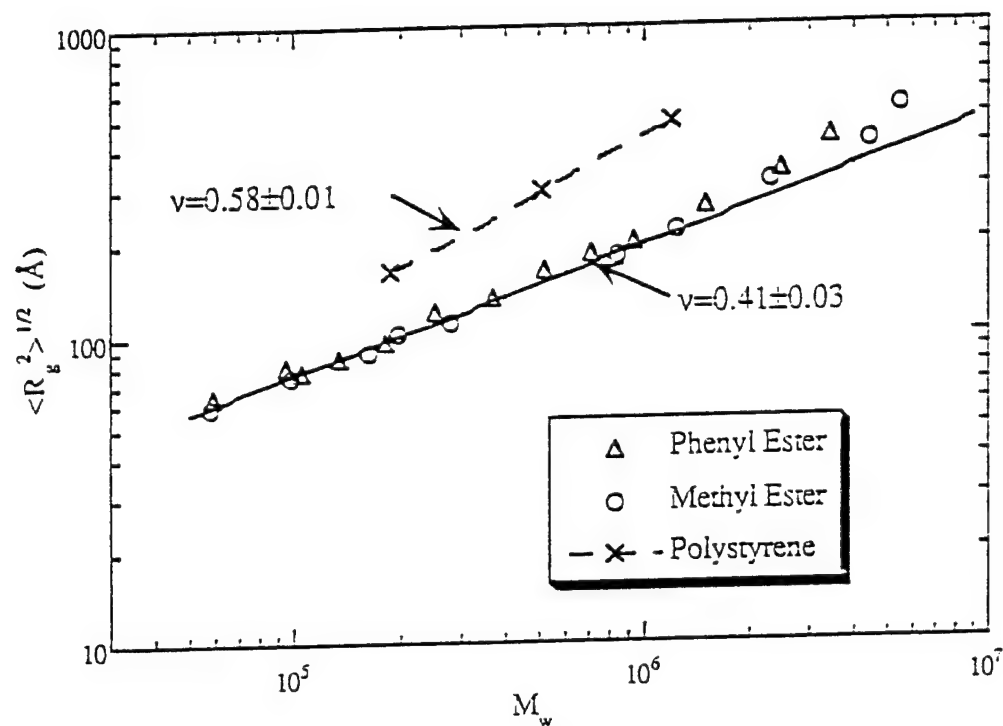
initial unit



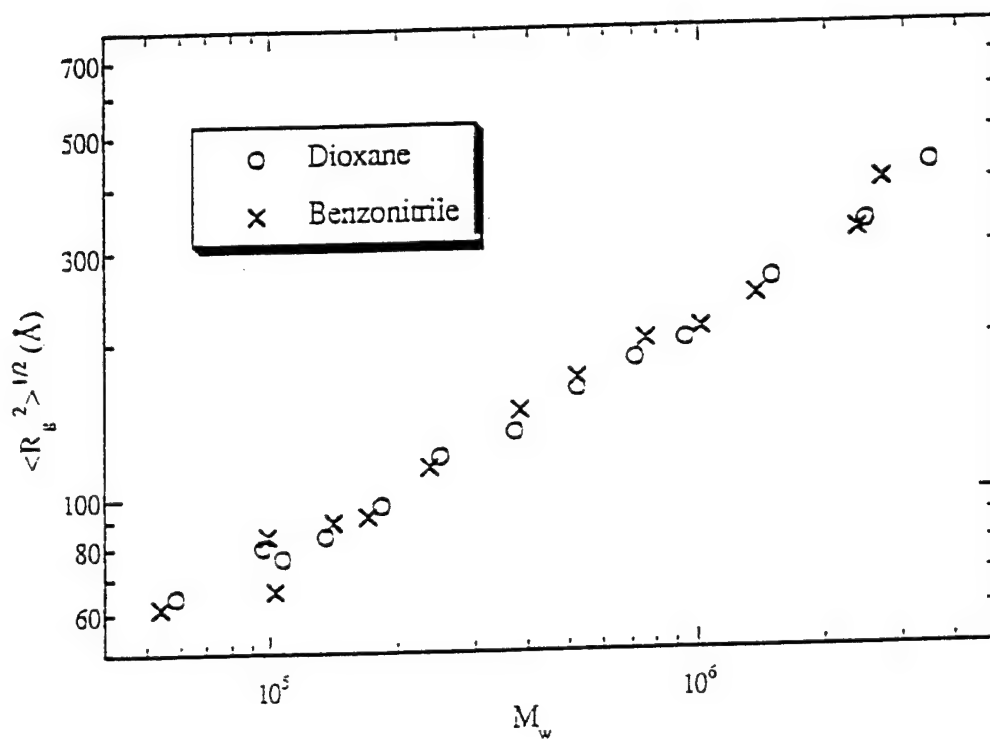
^1H NMR peak identification of aromatic protons of EHP



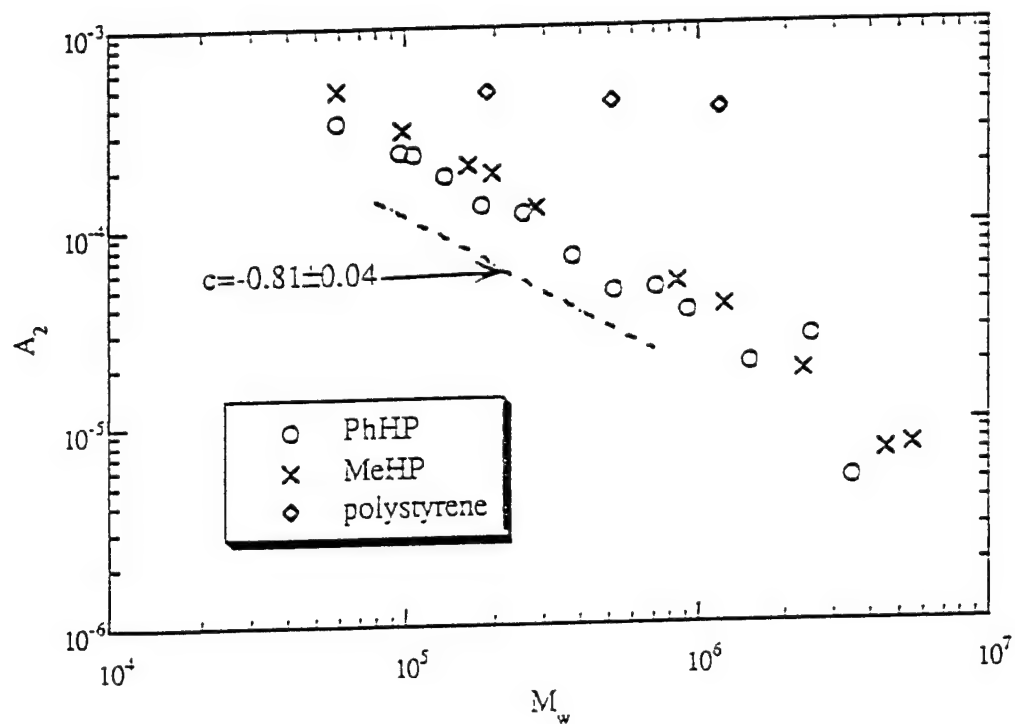
Dependence of degree of branching on degree of polymerization



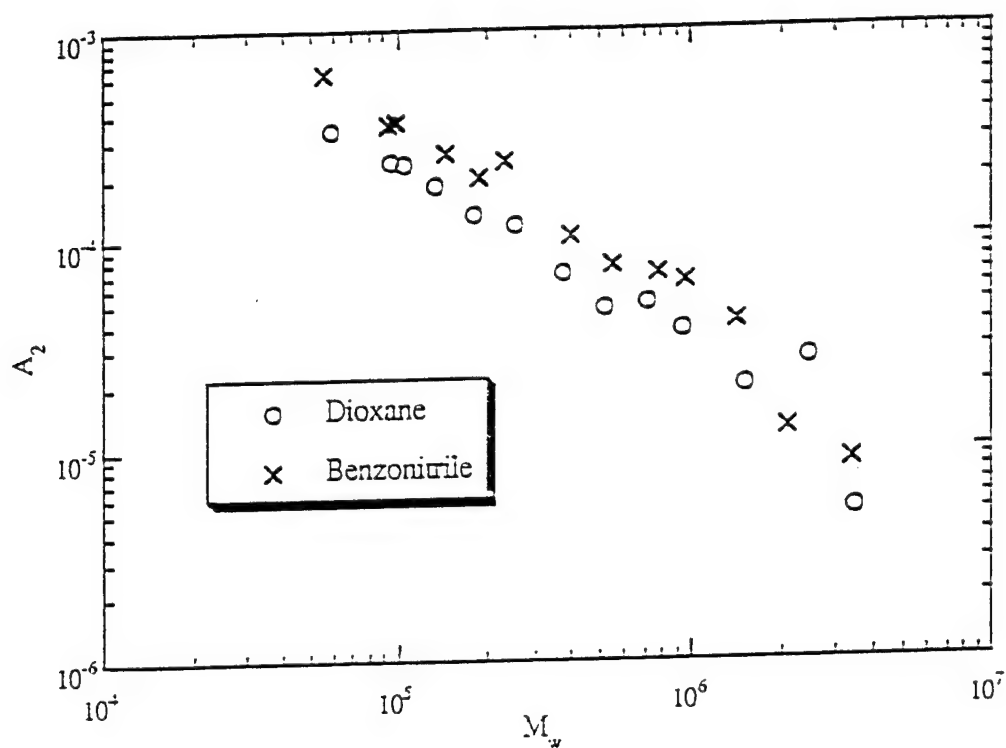
Dependence of root mean square radius of gyration $\langle R_g^2 \rangle^{1/2}$ on weight average molecular weight (M_w) (measured in dioxane at 15°C)



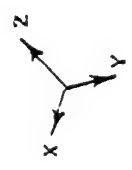
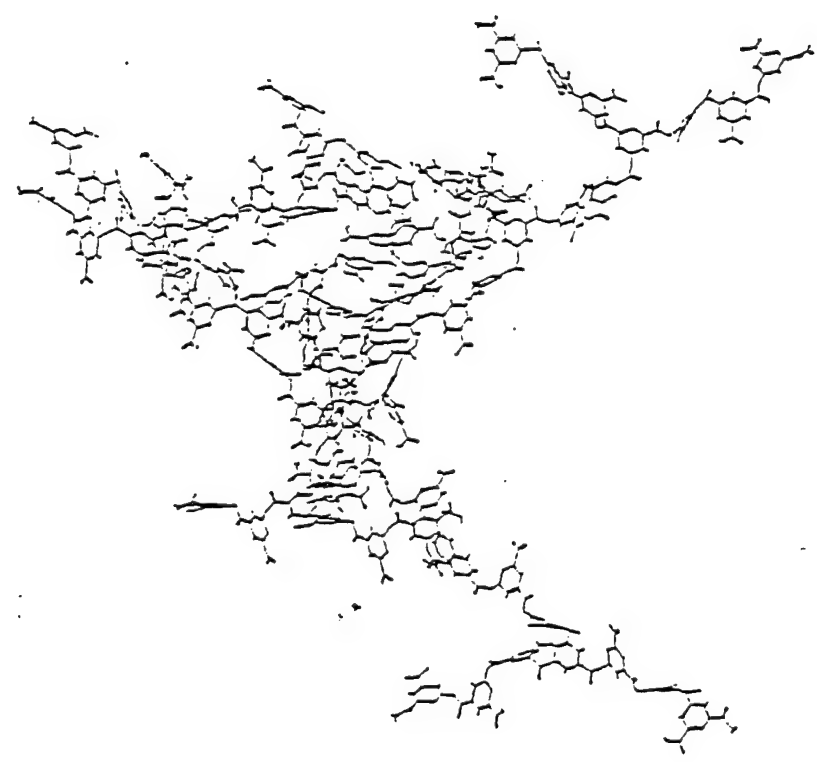
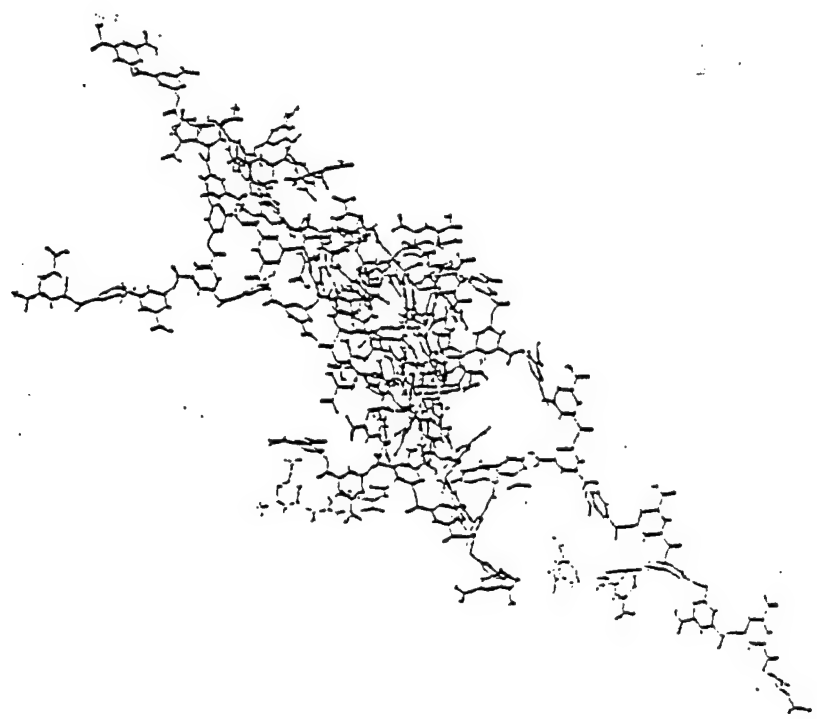
Dependence of root mean square radius of gyration $\langle R_g^2 \rangle^{1/2}$ on weight average molecular weight (M_w) (Measured with MeHP at 15°C)



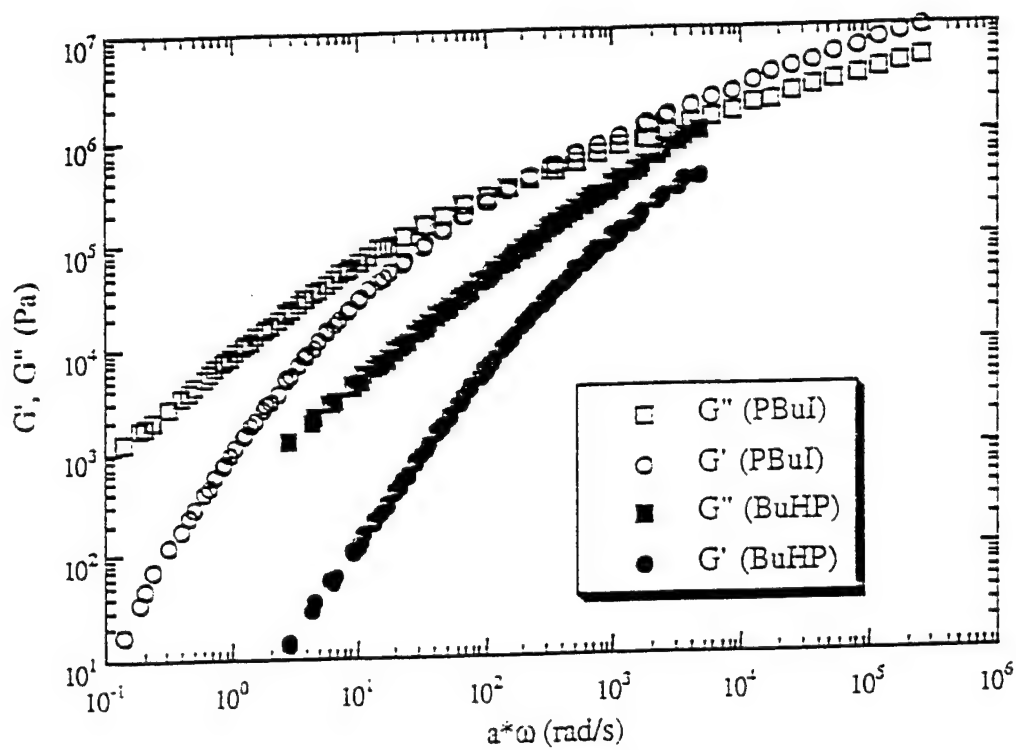
Dependence of the second virial coefficient (A_2) on weight average molecular weight (M_w) (measured in dioxane at 15°C)



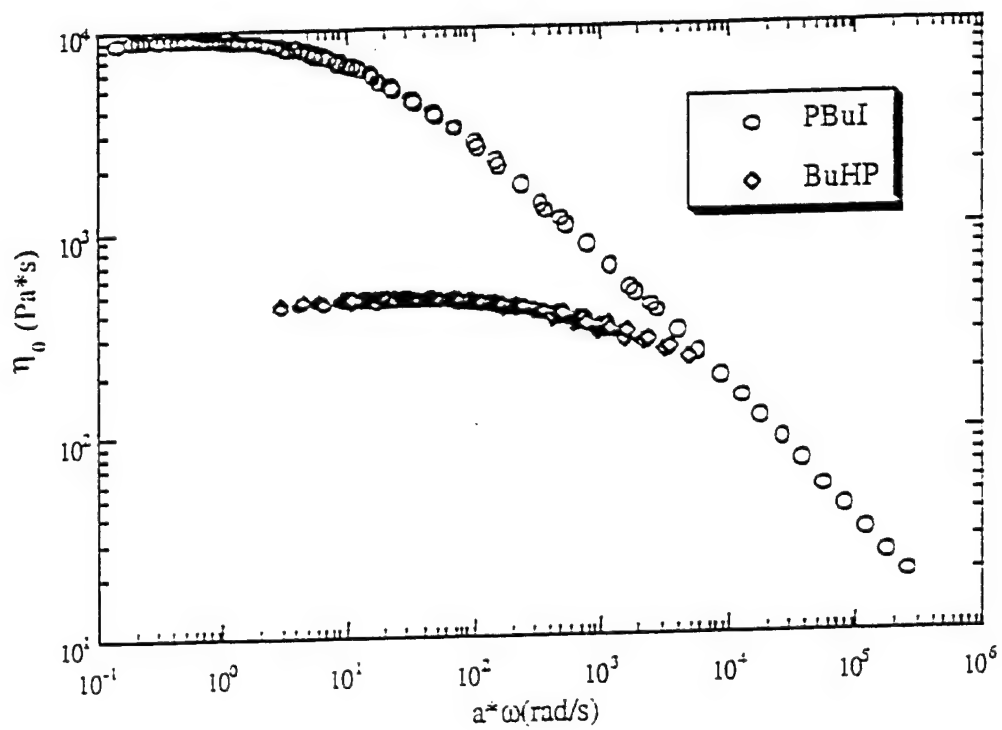
Dependence of the second virial coefficient (A_2) on weight average molecular weight (M_w) (measured with MeHP at 15°C)



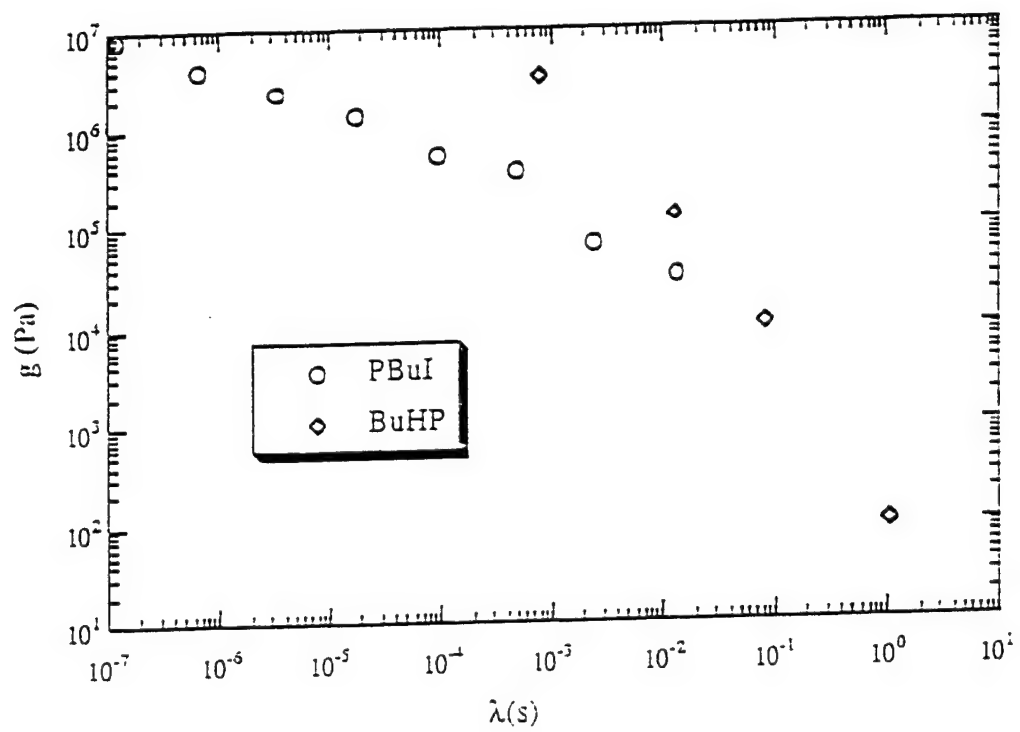
Molecular simulation results



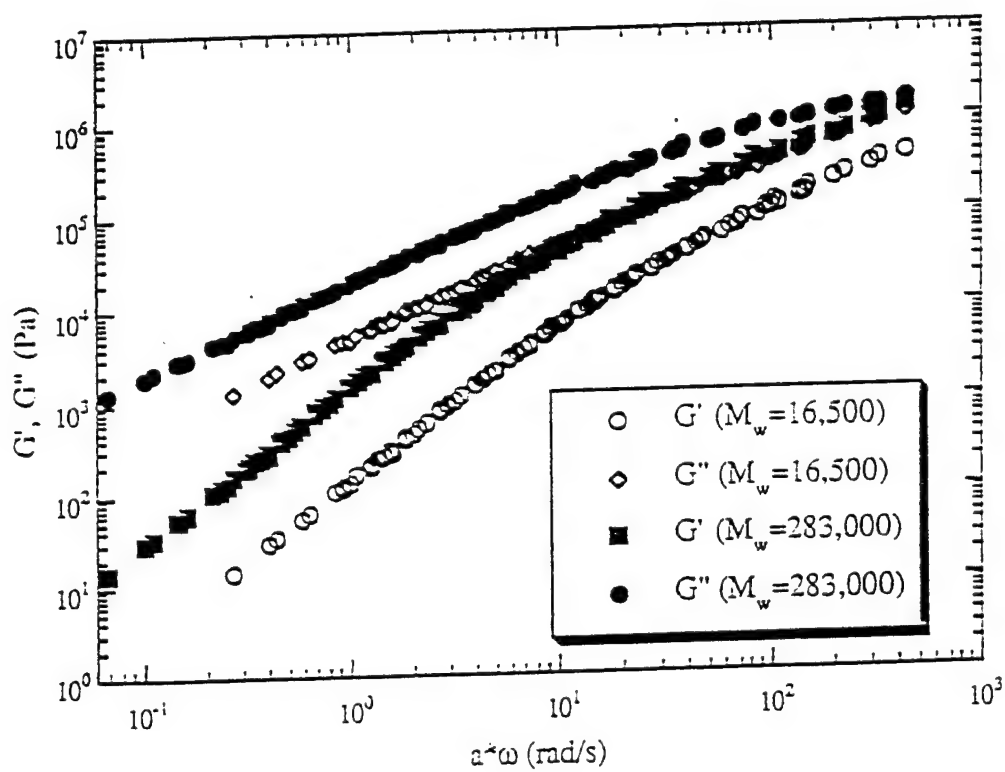
Mastercurves of BuHP and PBuI ($T_{ref} = T_g + 80^\circ\text{C}$)



Dynamic viscosity of BuHP and PBuI ($T_{ref} = T_g + 80^\circ\text{C}$)



Relaxation spectra of BuHP and PBuI



Mastercurves of BuHP of $M_w = 16,500$ and $283,000$ ($T_m = 120^\circ\text{C}$)

The effect of hyperbranching topology on the miscibility and compatibility of blends containing these materials was also studied. For example, the miscibility of BuHP and poly 1,4-butylene isophthalate (PBuI) was investigated thermally, by TEM and in terms of rheological parameters.

Thermal experiments for blends with BuHP contents from 0 to 100% in 10% increments and annealing temperature ranged from 80 to 200°C were carried out. For the blends that were composed of BuHP of $M_w = 16,500$ and PBuI of $M_w = 18,300$, immiscibility at all annealing temperature was found.

Thus blends of n-butyl hyperbranched polyarylate and its linear analog poly(1,4-butylene isophthalate) were found to be immiscible. Because the positive enthalpy had been minimized by the choice of this model system, the deciding factor for immiscibility is attributed to the unfavorable entropy change of mixing. A lattice model was proposed to explain the immiscibility in these systems. Apparently, it is necessary to introduce specific interactions between the two polymer component to possibly form a miscible blend. However, the blend can be compatible if the chemical composition of the two constituent polymers are similar. As a result of compatibility, the viscosity of blends show negative deviations from an additive relation. This property opens applications for hyperbranched polymers as rheology modifiers.

G. New Polymers; Miscellaneous Studies (2, 4, 7, 8, 13, 15, 39, 56, 57, 61, 67)

The results of a number of AFOSR-supported investigations which do not fit the above categories have appeared. These include the syntheses of new high temperature polymers based on novel polyimide and benzoylamine imide structural

elements. A number of theoretical studies have addressed issues of the solid liquid and surface states of polymers particularly with respect to transition phenomena while others have continued earlier extensive Monte Carlo simulations of polymer mixtures under a variety of conditions. In all cases the results are fully described in the respective publications.

VIII. PUBLICATIONS IN PERIOD WITH AFOSR SUPPORT

Eighty-two scientific papers (76 published, 6 in press) and one patent were completed with full or partial AFOSR support during the grant period.

1. J. Chem. Phys. 98, 712-716 (1993) (with G. Mao, J.E. Fischer and M.J. Winokur) "Nonplanarity and Ring Torsion in Poly(*p*-phenylene vinylene): A Neutron-Diffraction Study".
2. J. Appl. Polym. Sci., 47, 753-760 (1993) (with S. Li) "Preparation and Characterization of Aromatic Polyimides and Related Copolymers".
3. Macromolecules, 26, 287-297 (1993) (with I. Teraoka and K.H. Langley) "Diffusion of Polystyrene in Controlled Pore Glasses: Transition from the Dilute to the Semidilute Regime".
4. J. Appl. Polym. Sci., 47, 1419-1425 (1993) (with N.S. Schneider and J.L. Illinger) "The Interaction of Water with Polyurethanes Containing Block Copolymer Soft Segments".
5. Macromolecules, 26, 539-544 (1993) (with C.T. Imrie, T. Schlee and G.S. Attard) "Dependence of the Transitional Properties of Polystyrene-Based Side-Chain Liquid-Crystalline Polymers on the Chemical Nature of the Mesogenic Group".
6. Macromolecules, 26, 545-550 (1993) (with C.T. Imrie and G.S. Attard) "Comparison of the Mesogenic Properties of Monomeric, Dimeric, and Side-Chain Polymeric Liquid Crystals".
7. Polymer International, 31, 197-206 (1993) (with N. Segudovic, R. Vukovic, V. Kuresevic and W.J. MacKnight) "Solution Properties of Poly(fluorostyrene-co-chlorostyrene) Copolymers. I. Light Scattering, Differential Refractometry and Viscometry".
8. Polymer International, 31, 207-212 (1993) (with N. Segudovic, R. Vukovic, V. Kuresevic and W.J. MacKnight) "Solution Properties of Poly(fluorostyrene-co-chlorostyrene) Copolymers. II. High-performance Gel Permeation Chromatography".
9. Polymer International, 31, 291-296 (1993) (with H. Fischer and W.J. MacKnight) "Structure in Mesogenic Diol-containing Polyesters".
10. Macromolecules, 26, 1188-1190 (1993) (with Z. Yang and I. Sokolik) "A Soluble

Blue-Light-Emitting Polymer".

11. Polymer, 34, 972-976 (1993) (with S. Cimmino, E. DiPace, E. Martuscelli and C. Silvestre) "Isotactic Polypropylene/Hydrogenated Oligo(Cyclopentadiene) Blends: Phase Diagram and Dynamic-mechanical Behaviour of Extruded Isotropic Films".
12. Polymer, 34, 1449-1453 (1993) (with R. Vukovic, M. Zuanic, G. Bogdanic and V. Kuresevic) "Miscibility in Blends of Sulfonfylated Poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) with Homopolymers of Halogen-substituted Styrene Derivatives".
13. Physical Review E, 47, 1108-1118 (1993) (with I. Teraoka) "Glass Transition and Dynamic-mobility Spectrum of an Isotropic System of Rodlike Molecules".
14. Progress in Colloid & Polymer Science, 91, 153-155 (1993) (with K. H. Langley and I. Teraoka) "Diffusion of Flexible and Semirigid Polymers Confined to the Pore Spaces in Porous Glass".
15. J. Appl. Polym. Sci., 48, 1023-1033 (1993) (with L. Litauszki) "New Poly(bisbenzoylamine imide) Series: Synthesis and Characterization".
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